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Application of Electrical Spin Resonance in Chemical Kinetics

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The application of electron spin resonance (ESR) in the study of the kinetics of chemical reactions involving free radicals and paramagnetic ions is a very promising and rapidly developing field of study. In the first part of the review certain theoretical aspects and latest advances in studies on the kinetics of chemical reactions by the ESR method are discussed. Particular attention has been given to methods of analysis of the ESR spectra of free radicals, to methods for the calculation of concentrations, and also to a new method for the determination of local concentrations of paramagnetic centres from the dipole-dipole contribution to ESR line width.
In the second part of the review examples of the application of electron spin resonance in chemical kinetics are examined, and studies on radical reactions and the cage effect in solid matrices, and also measurements of steady-state concentrations of active radicals directly in the course of chemical reactions are discussed in detail.

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I. INTRODUCTION

This review was written on the suggestion of the late V. V. Voevodskii, one of the first scientists to understand the exceptionally great promise of the application of electron spin resonance in chemical studies. Thanks to him, Soviet science now occupies a leading place in the field of chemical ESR spectroscopy.

The application of radiospectroscopic methods, nuclear magnetic resonance (NMR), and electron spin resonance (ESR) led to significant advances in studies on the fundamental problems of theoretical and applied chemistry. Radiofrequency techniques enable often hitherto unobtainable information about the structure of matter and the dynamics of the processes occurring in it to be obtained. In particular, electron spin resonance

permits the observation of signals (arising as a result of the absorption of energy on transitions between Zeeman sublevels) from unpaired electrons; the actual carriers of such electrons may be a wide variety of paramagnetic centres (PC)—atoms, molecular fragments (free radicals), molecular ions, individual paramagnetic ions, solid-state defects, molecules in the triplet state, etc. On the other hand, real chemical processes usually take place via a series of fundamental intermediate stages, with participation of chemically active valence-unsaturated species—radicals, ions, etc. Thus the ESR method is, as it were, specially suitable for the study of the mechanism of chemical reactions, because such study in fact consists in the identification and quantitative investigation of the sum total of intermediate processes.

One of the valuable features of the ESR method is the fundamental ease of the quantitative measurement of the effect: in the absence of saturation, the total intensity of the absorption lines is proportional to the number of absorbing species, the spectroscopic absorption coefficients being the same for the majority of paramagnetic centres. Furthermore, the ESR method is sensitive only to paramagnetic centres, regardless of the remaining species in the system, which leads to high sensitivity of the method, permitting the detection of paramagnetic centres at concentrations of 10^{-10}–10^{-11} M. However, the value of the ESR method does not lie solely in the quantitative detection of signals from paramagnetic centres. The interaction of an unpaired electron with paramagnetic nuclei and neighbouring electrons and the dependence of these interactions on the geometry of the species and internal motions are all reflected in the ESR spectrum in the form of a hyperfine structure (HFS), fine structure, line broadening due to relaxation, displacement of the positions of the lines, etc. The physical principles of electron spin resonance and nuclear magnetic resonance are now widely known and it is therefore unnecessary to dwell on these problems. The above features of the ESR spectrum permit an approach to the determination of the true structures of complex paramagnetic centres, the details of their geometry, the distribution of unpaired electron density among various functional groups, and can even provide information about the interaction of the paramagnetic centres with the surrounding medium and the internal motions in the medium.

Nowadays several dozen papers on the study of chemical problems by the ESR method are published every month. The ESR method is used in a wide variety of chemical fields—organic chemistry, electrochemistry, radiation chemistry, polymer chemistry, quantum chemistry, chemical kinetics, and catalysis. It would clearly be unreasonable to attempt to describe all the aspects of the chemical applications of electron spin resonance. However there is one problem which combines all the studies in this field—the problem of the extraction of "chemical" information from ESR spectra. With the existing experimental techniques, it is relatively easy to detect the ESR spectra of a wide variety of chemical systems, but it is much more difficult to interpret correctly these spectra and to obtain from them the chemical information concealed in the various features of the hyperfine structure and the line form of the signal. Certain fundamental problems of the analysis of ESR spectra from the standpoint of obtaining "chemical" information will therefore be discussed in the first part of the review.

In the second part the use of electron spin resonance to study the kinetics and mechanism of chemical reactions will be mainly examined. The use of electron spin resonance in the investigation of the kinetics and mechanism of reactions is one of the most important and most interesting aspects of the application of this method.

Chemical applications of electron spin resonance outside the scope of this theme can be roughly characterised as structural–chemical studies. A much larger number of reviews and monographs have been devoted in recent years to these investigations than to studies on the kinetics and mechanism of reactions.

II. ANALYSIS OF ESR SPECTRA

In chemistry, the analysis of ESR spectra should usually provide an answer to the following questions[1]: (1) what paramagnetic centres are formed under particular conditions; (2) what is the concentration of these centres and how does it vary under different conditions; (3) what is the distribution of spin density of the unpaired electron in the active centre; (4) in what way does the unpaired electron interact with the surrounding medium, etc.

In order to calculate the concentration of paramagnetic centres, it is necessary to calculate the area under the absorption curve and to compare it with the area under the signal from a standard (with a known number of paramagnetic centres). Such standard signals may be provided by stable radicals (diphenylpicrylhydrazyl, diphenylnitric oxide, etc.) and ions [manganese(II) compounds, $CuCl_2.2H_2O$ crystals, etc.] Here the most difficult problem is the calculation of the area and, in some cases, the evaluation of the absorption coefficient.

To obtain an answer to the remaining questions, it is in general necessary to perform an analysis in two consecutive stages—formal mathematical and then quantum-chemical analysis of the spectrum. In the first stage one must establish from the experimental spectrum, which may consist of a large number of weakly resolved lines, which interaction determines the formal spectrum, i.e. one must usually establish with which nuclei the unpaired electron reacts, what are the interaction constants, line widths, etc.

In the second stage, using quantum-chemical relations, it is possible to establish the structure of the radical, the distribution of spin density, and the nature of the motion of certain functional groups. There is an extensive literature on this question, including reviews and textbooks, and therefore it will be considered only briefly. The problems of the formal mathematical analysis of the spectra will be discussed in greater detail. Although the creation of effective methods for the mathematical analysis of complex ESR spectra is absolutely essential for the successful application of this method, detailed studies of the problems of formal mathematical analysis developed only very recently.

1. Determination of Average Absolute Concentrations

In principle this is a simple problem. The integral intensity of the ESR signal is proportional to the number of paramagnetic centres, consequently in the simplest case, when there is a standard with a known number of unpaired electrons N_{st}, we have

$$N_{sp} = N_{st}\frac{S_{sp}}{S_{st}},$$

where S_{sp} and S_{st} are the areas under the ESR absorption curves for the specimen and the standard respectively. Since the signal is usually recorded in a differential form,

the calculation requires graphical integration. One can use the relation

$$S = \int_{-\infty}^{\infty} I(x)\,dx = \Big|_{-\infty}^{\infty} xI(x) - \int_{-\infty}^{\infty} xI'(x)\,dx\,. \qquad (1)$$

Since the first term on the right-hand side of Eqn. (1) is zero both for the Lorentzian and Gaussian line forms, Eqn. (1) permits the replacement of double integration by a single determination of the first moment of the spectral line.

The last operation was further facilitated[2] by the introduction of nomograms consisting of a family of hyperbolae $xI' = C_i$. After the superposition of the nomograms on the spectrum, the integration reduces to adding together the values of C_i corresponding to the experimental curve (see Fig. 1). The accuracy of such treatment is 20–30%,

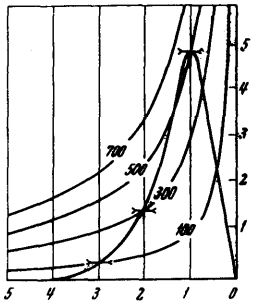


Figure 1. Diagram illustrating the use of a nomogram for the calculation of the first moment of the ESR line[2]; $S = 2(100 + 300 + 500) = 1800$ arbitrary units.

as in graphical integration. It is then found[3] that the integration step Δx should not be made too small, a sufficient condition is $\Delta x < \frac{1}{2}\Delta H_u$. The blurring of the hyperfine structure due to modulation is not reflected in the value of S. Furthermore, S does not depend in principle on the starting point of the calculation (but the accuracy is greater if the starting point of the calculation coincides with the true centre of the spectrum). However, the greatest error can be introduced by the superposition of a "parasitic" line due to the drift of the zero or due to the presence of a paramagnetic background. To take this superposition into account it is necessary to recover the background line, to determine the first moment for the latter, and to subtract the result from $M_{1\,\mathrm{exp}}$. If it is assumed that the zero shift is linear, then it is easy to show that

$$M_{1\,\mathrm{drift}} = 2\int_0^{\infty} \frac{\Delta I_0'}{2\Delta H_0}\,HdH = \frac{1}{3}\Delta I_0'(\Delta H_0)^2$$

and

$$S = M_{1\,\mathrm{exp}} - \frac{1}{3}(\Delta H_0)^2\,\Delta I_0'\,,$$

where ΔH_0 is the distance from the zero line to the last point of the integration and $\Delta I_0'$ is the total zero shift (see Fig. 2). In some cases one can determine the area more simply from the formula

$$S = \alpha\varkappa\Delta H_{\frac{1}{2}}^2 I_m'$$

where $\alpha = \Sigma A_i/A_m$ (A_i are the intensities of the hyperfine structure components) and the line form coefficient is

$$\varkappa = \begin{cases} \pi/\sqrt{3} & \text{for Lorentz line form} \\ \frac{1}{4}\sqrt{\frac{\pi e}{2}} & \text{for the Gaussian line form.} \end{cases}$$

Since the form and width of an individual line are not usually evident, the empirical coefficient is preferred:

$$\varkappa_{\mathrm{eff}} = S/I_m'\,. \qquad (2)$$

When a large series of measurements is made, one can determine κ_{eff} at only a few reference points and at the remaining points the area S can be measured on the basis of I_m' and the value of κ_{eff} interpolated for the given point (see Fig. 3).

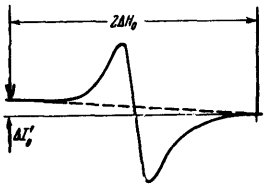


Figure 2. Diagram illustrating how the shift of the zero line is taken into account in the calculation of the first moment.

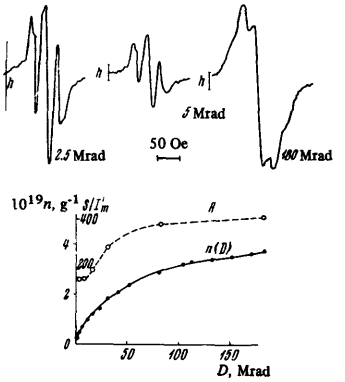


Figure 3. An example of the construction of the kinetic curve on the basis of ESR data (kinetics of the accumulation of free radicals in the low-temperature β-radiolysis of glycine); A—calibration curve for the determination of the ESR line form coefficient.

Additional difficulties arise when the standard and the specimen differ in the effective spin S, temperature, g-factor, etc. The spin and temperature can be easily taken into account, since

$$S \sim N\,\frac{S(S+1)}{T}\,.$$

When there is a considerable difference between the g-factors, it is necessary to take into account the difference between the probabilities of the transition.

We shall now discuss two examples, which are important in practice, of the calculation of the absolute concentrations of paramagnetic centres for which the absorption

coefficients differ significantly from the coefficients for the free spins. The existing theoretical formulae for signals from triplet molecules with $g = 4(\Delta M_S = 2)$ are complex and inaccurate. Alfimov et al.[4] proposed a novel method for the determination of the number of triplet centres based on recording by the ESR method the time of the increase and fall of the intensity of the signals from the triplets. On the basis of the simplest kinetic mechanism,

$$M_0 \xrightarrow{\beta j} M_\tau ,$$
$$M_\tau \xrightarrow{1/\tau} M_0 ,$$

the curve for the accumulation of triplets under the action of a beam of electrons with an intensity j is given by

$$N_\tau = N_0 \frac{\beta j}{\beta j + 1/\tau} \{1 - \exp[-(\beta j + 1/\tau) t]\} \qquad (3)$$

and, after the beam is switched off, the steady-state concentration becomes

$$(N_\tau)_{cr} = \frac{\beta j N_0}{\beta j + 1/\tau} .$$

From Eqn. (3), the time constant for the accumulation of triplets is

$$\tau_a = \frac{1}{\beta j + 1/\tau} .$$

On eliminating βj from the last two equations, we obtain

$$(N_\tau)_{st} = N_0 \left(1 - \frac{\tau_a}{\tau}\right) .$$

Finally specific difficulties arise in the identification and determination of the concentrations of free atoms (except H atoms) and radicals in the gas phase. Here, in contrast to a condensed phase, the orbital motion of the electrons may not be frozen and therefore the g-factors and spectroscopic absorption coefficients are significantly smaller and larger than for the condensed phase and vary from species to species. Furthermore, the spectra of di- and poly-atomic radicals show a rotational structure which leads to a very complex system of ESR lines, spreading over a range of several kilo-oersteds; however, as a rule it is possible to record only part of these lines. In this connection, the determination of the absolute concentrations of species in the gas phase requires special calculations every time. The first such calculation, the aim of which was to calibrate O against O_2, was performed by Krongebb and Strenberg[5]. Later calibration calculations for OH against NO and for halogen atoms against O_2 were performed independently by Nalbandyan et al.[6] and by Westenberg[7]. In such calculations account is taken of the fact that the absorption in OH, NO, etc. is due to electric dipole transitions. The resonator is usually completely filled with the gas, so that the paramagnetic OH species come within the region of the antinode of the electric field and the NO used as standard permits automatic allowance for the effect of the configuration of the fields. However, if the measurements are made at high temperatures, considerable temperature differences always appear in the resonator, and nitric oxide cannot be used, since its signal depends markedly on temperature. In these cases Nalbandyan and coworkers[6] use molecular oxygen as an intermediate standard.

2. Measurement of Local Concentrations of Paramagnetic Centres

The methods for the determination of the number of paramagnetic centres by the ESR method have already been examined. On dividing this number by the volume of the specimen, we can always determine the average concentration of paramagnetic centres in the specimen. However, this quantity can be usefully employed in physicochemical calculations only when it is certain that the distribution of paramagnetic centres throughout the volume is uniform (equally probable). If we are dealing with a gas or liquid phase, such a problem does not arise—here the distribution of all the active centres is homogeneous. However, in a solid phase and in heterogeneous systems it is easy to imagine a non-uniform distribution of paramagnetic centres —such non-uniformities can arise from radiation tracks on irradiation, phase separation on freezing, active sites on the surface, etc. Here the study of the intensity of the signal is of no avail and it is necessary to seek other ways of estimating the true density of paramagnetic centres. In principle, one can use the fact that, at the concentrations usually recorded by the ESR method, the average distance between paramagnetic centres is such that their dipole–dipole interaction should influence the form of the spectrum (0.1–1 Oe). According to fairly simple calculations[8,9], there is a relation between the dipole–dipole contribution to line width between the points of maximum slope and the concentration of paramagnetic centres (for $n < 1\%$, which is always the case in chemical studies):

$$\Delta H_i(\text{Oe}) = Bn\ (\text{cm}^{-3}), \qquad (4)$$

where

$$B = \begin{cases} 5.4 \times 10^{-20}\ \text{Oe cm}^3 \text{ (random distribution, Lorentz line form)} \\ 4.9 \times 10^{-20}\ \text{Oe cm}^3 \text{ (uniform distribution, Gaussian line form).} \end{cases}$$

If this interaction determines the apparent line width, the problem may be regarded as solved. Wyard[9] observed directly in irradiated frozen solutions of hydrogen peroxide the variation of line width with concentration (i.e. the area of the signal). According to his estimate[9], $B = 7.5 \times 10^{-20}$ Oe cm^{-3}. In this case the ESR signal consists of a single line. For complex ESR spectra the detection of line broadening appeared at first to be a hopeless task, but thorough analysis of the accumulation curve recorded up to large doses enabled the present author together with Mikhailov[10] to detect the broadening of the hyperfine structure components at average concentrations of the order of 10^{19} cm^{-3} (Fig. 4). The quantity $\sqrt{\kappa_{\text{eff}}}$, where the line form coefficient κ_{eff} was determined from Eqn. (2), served as a measure of the width ΔH_i of an individual component. For complex spectra, this method proved to be more sensitive than the direct measurement of line width or the calculation of the second moment. The undefined multiplier in the formula $\Delta H_i = \beta\sqrt{\kappa}$ was determined for the most highly resolved signal with the aid of the "Atlas of ESR Spectra". Fig. 4 shows that ΔH_i increases linearly with the average concentration n (this can be regarded as proof of the dominant contribution of spin–spin interaction to ΔH_i), and n_{loc} exceeds n significantly but increases together with the latter. Thus here the hyperfine structure components are homogeneous. In the most complex case of non-homogeneous lines, consisting of a large number of unresolved spin packets, ΔH_i in Eqn. (4) must be replaced by the width of the spin packet ΔH_S. The relaxation characteristics of the ESR signal obtained by the spin-echo or successive saturation methods have begun to be used recently for the determination of ΔH_S.

The application of the spin-echo method (based on Hann's principle[11,12]) in the study of free radicals in solid matrices was first described by Raitsimiring et al.[13] Despite certain theoretical difficulties in the interpretation of the experimental data, this method is extremely promising.

In particular, it is also evident from the results of Raitsimiring et al.[13] that the local radical concentration measured from ΔH_S increases in parallel with the average concentration, remaining higher than the latter in a number of cases.

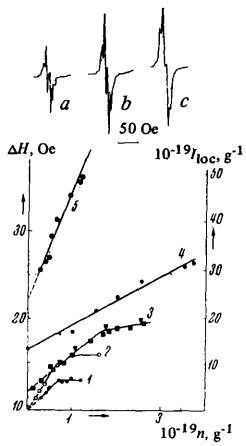


Figure 4. Variation of the width of the hyperfine structure components of the ESR spectra of irradiated substances with the average concentration (i.e. radiation dose):
1) cytidine; *2*) guanosine; *3*) thymine; *4*) glycine; *5*) DNA.

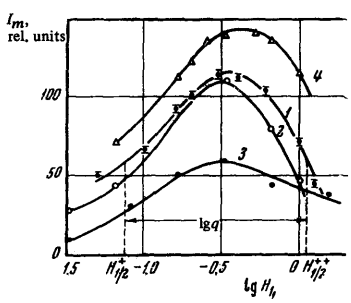


Figure 5. Example of the analysis of microwave saturation curves; variation of the intensity of the ESR signal in irradiated substances with the power of microwave detector[14] (77°K):
1) α-alanine; *2*) guanine hydrochloride; *3*) phenol; *4*) glycine.

The present author initiated a simpler (but less sensitive) method for estimating ΔH_S from the width of microwave saturation curve[14] based on the theory of inhomogeneous saturation of Portis[15] and Castner[16]. Some of the results[14] are presented in Fig. 5. At saturation the homogeneous line broadens because its centre is saturated to a greater extent than the edges, so that, when the power applied is high, the intensity of the signal falls to zero. If the effective width of an inhomogeneous line $\Delta H^* \gg \Delta H_S$, an increase of ΔH_S will not affect ΔH^* and the intensity of the signal will cease to depend on the amplitude of the microwave field H_1, i.e. the width $\lg q$ of the $I'_m - \lg H_1$ saturation curve becomes infinite. Theoretical calculation of saturation curves for various $\Delta H^*/\Delta H_S$ makes it possible to plot a calibration curve: $\Delta H^*/\Delta H_S = f(q)$. Such a calculation has been performed by Castner[15] and then used for estimating ΔH_S.[17,18] However, Castner's calculation[15] was made for an ESR spectrometer without magnetic modulation and this was not stated. Zhidkov et al.[14] carried out the calculation for the usual experimental conditions (modulation of the magnetic field with an amplitude $\Delta H_S \leq \Delta H_M < \Delta H^*$; in view of the slow-pass conditions obtaining the modulation frequency $\nu_M \ll 1/T_1$; in the experiments[14] $\nu_M = 333$Hz). Then for $q < 50$ the calibration relation is described by an almost linear function

$$\frac{\Delta H^*}{\Delta H_S} \simeq 0.72\,q - 6.15\,,$$

In the experiments, apart from the cases where $n_{loc} \gg n$, the equality $n_{loc} \simeq n_{av}$ was obtained for certain specimens, which may be regarded as confirmation of the validity of the calculation. In the general case the theoretical interpretation of continuous saturation curves is also quite difficult, since the calculations were made on the assumption of non-interacting spin packets (i.e. the absence of spectral diffusion) and without taking into account the contribution of exchange interaction. (It has now been shown that at concentrations less than 10^{20} cm^{-3} the exchange contribution to line width may be disregarded).

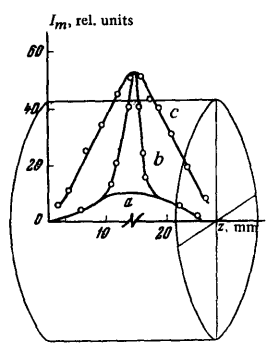


Figure 6. Distribution of sensitivity in an ESR resonator:
a) in the normal case; *b*) in a resonator with a spiral nozzle;
c) in a resonator with mobile packing[19].

In connection with the measurement of the concentrations, it is interesting to consider briefly also the following problem. The microwave resonator usually consists of a "transducer" with a linear dimension of about 30 mm (*X*-range) or 8 mm (*K*-range) and therefore if the measurements are on an extended volume (paramagnetic centres in a jet, in a gas mixture, etc.), we can determine only the concentration averaged over the resonator. We believe that an interesting possibility for the determination of local concentrations at a "point" with dimension smaller by a factor of 10 than that of the resonator arises from the effect, observed by the present author together with Taranukha, involving the localisation of the microwave power by a spiral section[19]. It was found that, when one or two turns of a conducting spiral are placed along the antinode of the lines of force H_1, then it is possible to obtain at the location of the spiral a δ-flash of microwave power, so that the instrument begins to "see" virtually only whatever is located in the zone of its spiral (see Fig. 6). Measurements on model objects confirmed this possibility, but a very unfavourable feature of this system is the necessity for a spiral of very small diameter (1–2 mm for a 3 cm resonator).

3. Formal Mathematical Analysis of ESR Spectra

The ESR spectrum is a system of lines, the derivation of chemical information from which constitutes a special task. For chemically active species (free radicals) the complexity of the spectrum is usually due to the hyperfine structure (i.e. the interaction of the unpaired electron with the nearest paramagnetic nuclei) and also the anisotropy of the hyperfine structure and the positions (g-factor) of the lines. Two stages are required for the identification of the paramagnetic centres: (1) one must establish with which nuclei (and with what constants) the unpaired electron interacts; (2) on the basis of the findings in the first stage, one must establish, using the methods of quantum chemistry, the chemical structure of the paramagnetic centre and, as far as possible, its geometrical structure and the distribution of the spin density of the unpaired electron.

We shall consider initially a spectrum consisting of well—resolved lines (i.e. line width $\Delta H_i < a_{\min}$). This spectrum must correspond to a system of levels (under the conditions of a strong field):

$$\Delta E = g\beta H + \sum_k a_k I_{z_k} \ ,$$

where a_k are hyperfine structure constants and I_{zk} the projections of the nuclear spins.

As a result of the interaction of the unpaired electron with the kth nucleus, $2I_k + 1$ lines are produced, and if there are N nuclei, the number of lines is $\prod_{k=1}^{N} (2I_k + 1)$. These lines are distributed in such a way that the distances from the extreme line to the others are a_1, a_2, a_3, ...; $a_1 + a_2$, $a_2 + a_3$ ...; $a_1 + a_2 + a_3$, ... etc. (see Fig. 7).

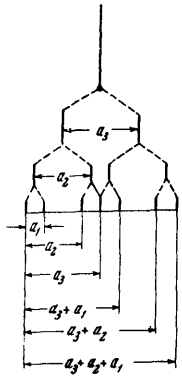


Figure 7. Diagram illustrating the formation of the hyperfine structure (splitting by three protons with $a_1 : a_2 : a_3 = 1 : 3 : 4$).

Therefore it is readily seen that the hyperfine structure of the ESR spectrum can be represented by the polynomial

$$\prod_{k=1}^{k_m} (1 + z^{\alpha_k})^{S_k} \quad \text{for } I = 1/2$$

$$\prod_{l=1}^{l_m} (1 + z^{\alpha_l} + z^{2\alpha_l})^{S_l} \quad \text{for } I = 1 \text{ etc.}$$

where α_k represents the different splittings measured in relative units ($\alpha_k = a_k/a_{\min}$) and S_k the number of nuclei for which $a = a_k$, i.e. the multiplicity of the degeneracy. After carrying out the multiplication, we obtain a polynomial $\Sigma A_m z^m$, in which the coefficients A_m correspond to the relative line intensities (the multiplicity of the degeneracy) and the exponents to their distances from the first left-hand line in units of $a_{\min}$. In particular, for n equivalent protons the characteristic polynomial is $(1 + z)^n$, which corresponds to $n + 1$ lines with a binomial distribution of intensities. Such formalised representation of the hyperfine structure makes it possible to formulate the problem of the analysis of the spectrum. The polynomial $\Sigma A_m z^m$ is known from experiments. The problem is how to recover from it the initial product. We shall examine, for simplicity, only nuclei with $I = 1/2$. The total number of lines is 2^N, where N is the number of nuclei, and therefore

$$N = \log_2 \frac{\Sigma A_i}{A_0} \ .$$

It is then clear from the structure of the characteristic polynomial that $A_1/A_0 = S_1$, the number of nuclei with minimum splitting. Finally the ratio of the total splitting in the spectrum to the smallest is

$$\frac{a^*}{a_{\min}} = \sum_{k=1}^{k_m} \alpha_k S_k \ .$$

In spectra corresponding to not more than two groups of non-equivalent nuclei, the number of these relations is sufficient for the determination of all the α_k and S_k. In the general case Dobryakov[20] obtained recurrent relations, from which all the α_k and S_k can be found from specified A_m. Thus the problem can be regarded as solved in principle (for $I = 1/2$), but since A_1 and a_1 (the intensity of the weakest component and the minimum splitting) enter into all the formulae, the above analysis is applicable only to relatively rarely encountered ideal "line" spectra.

Real spectra, particularly those of condensed phases, usually have line widths comparable to (or greater than) the minimum splitting. The method of trial and error has been used for a long time to analyse such spectra—a spectrum with a given structure is constructed taking into account the finite width and form (Lorentzian or Gaussian) of the individual line and the resulting curve is compared with experiment; when there is agreement, the theoretical spectrum yields a set of α_k and S_k values. Such construction is laborious and, in order to facilitate it, an atlas of theoretically calculated ESR spectra[21], containing a large set of spectra with various A_i and different resolutions ($\Delta H_i/a_{\min}$), was produced in 1962 at the Institute of Chemical Physics of the USSR Academy of Sciences. Experiments showed that the atlas causes the investigator to adopt fairly specific habitual procedures to interpret poorly resolved signals, but of course the atlas could embrace only a small part of line combinations encountered experimentally. At the present time there are specialised computers which can be used also for the synthesis of theoretical spectra. Finally the attempts to find the parameters of the theoretical spectrum by adjusting them on an electronic computer to fit the experimental spectra may be regarded as an improved version of the method of trial and error[22,23]. However, all this applies only to symmetrical multicomponent spectra, the description of which requires, apart from a set of S_k and α_k, the specification of only two parameters—$a_{\min}$ and ΔH_i. The line form due to the axial anisotropy of the g-factor is also described by only two parameters (Δg and H_i), and several studies have been devoted to the analysis of such lines[24-28].

In more complex cases where 3–4 or more parameters must be specified in order to describe the theoretical spectrum, the line form can be calculated only for definite sets of parameters specified *a priori*. Lefebvre and Maruani published recently a very complete programme for the computer calculation of spectra taking into account the splitting and the triaxial anisotropy of the g-factor and the hyperfine interaction[29]. The method of moments is also used for the analysis of poorly resolved ESR spectra[30]. However, the present author believes that the most logical formulation of the problem is analogous to that used by Dobryakov[20] for the analysis of line spectra. An attempt must be made to construct functional transformations, whereby the initial "physical" parameters of the spectrum can be found from its finite line form. It will be shown below on the simplest example that this can be done at least for spectra with a symmetrical hyperfine structure.

Let us examine the construction of the transformation, the reverse of the synthesis of the spectrum with a hyperfine structure, using a doublet as an example

$$F(x) = f(x+b) + f(x-b) \qquad (5)$$

where $b = \frac{1}{2}a_{\mathrm{H}}$. It is evident that

$$F(x+2b) = f(x+3b) + f(x+b)$$
$$F(x+4b) = f(x+5b) + f(x+3b),$$

where the left-hand side contains known functions. If we form an infinite series with alternating signs from $F(x+2kb)$, then all the terms on the right-hand side vanish except $f(x+b)$:

$$f(x+b) = \sum_{k=0}^{\infty} (-1)^k F(x+2kb). \qquad (6)$$

Thus, from the form of the envelope (apparent) of the lines, we can in principle find the form of the individual line (when b is known). The significance of transformation (6) can be readily elucidated from Fig. 8, which shows that, for sufficiently large k, the terms have virtually no effect on the pattern near $x = 0$. If b is unknown (and this is usually the case in the problem of spectral analysis), the following procedure can be used.

1. The right-hand side of Eqn. (6) is regarded as a function of x and b and preliminary differentiation of Eqn. (5) is carried out:

$$\Phi(x, y) = \sum_{k=0}^{\infty} (-1)^k F'(x+2ky).$$

Here y is a variable distance between the centres of the spectra and the terms of the summation have alternating signs. If $y = b$, then $\Phi(x, y) = f'(x+b)$. However, when $x = -b$, we have $\Phi(-b, b) = f'(0) = 0$ and therefore the function $\Phi(-y, y)$ has a remarkable property, namely it becomes zero when $y = b$. Hence it is possible to find b and then $f(x)$, i.e. to analyse the spectrum. This method of analysis was published by Newton et al.[31] The same method in principle was developed independently by Dobryakov and the present author[32], but in our version the analysis is carried out as follows.

2. It is clear from the scheme in Fig. 8*a* that, when the summation (5) is extended to $-\infty$, then along any section $0 \ldots y_0$ the modulus of the area under $\Phi(x, y_0)$ will become zero when $y = b$. Therefore we introduce the function

$$\psi_l(y) = \int_0^{ly} \left| \sum_{k=-\infty}^{\infty} (-1)^k F(x+2ky) \right| dx,$$

where l is an integral number which can be assumed to be 1 or 2 and the summation with respect to k can be carried out virtually from $-n$ to n, where $n \gg l$. This function becomes zero abruptly when $y = b$. Indeed, more rigorous treatment and model calculations showed[32] that, even for more complex cases, $\psi_l(y)$ is of the form shown in Fig. 8*b*, where a_N is the splitting of the nitrogen type, present in the spectrum of diphenylpicrylhydrazyl. Characteristic functions of a similar type can be constructed also for other values of I.

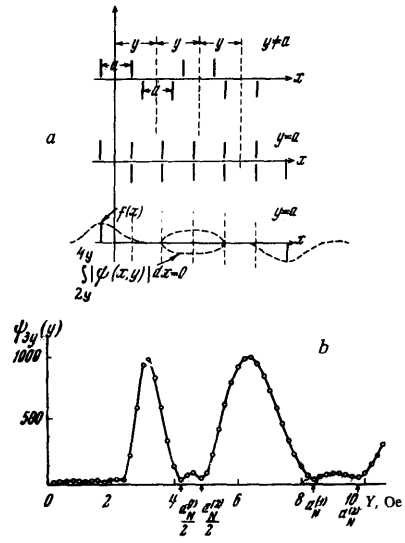


Figure 8. *a*) Diagram illustrating the analysis of a spectrum with a symmetrical hyperfine structure by the construction of the reverse transformation; *b*) analysis of the experimental spectrum of diphenylpicrylhydrazyl in dilute solution.

The method of Fourier transformations also opens up interesting possibilities for the analysis of ESR spectra[20,32]. Here the roots of the Fourier integral of the experimental function of line form are used to calculate the hyperfine structure constants.

The recently published "electronic" method for the sharpening of spectra by graphical differentiation or special magnetic modulation[33,34] and also of course the method of double electron–nuclear resonance[35] gives rise to specific possibilities in the analysis of poorly resolved spectra. However, all these procedures involve an appreciable loss of sensitivity in the recording of the signal.

In the identification of spectra the problem of how many different types of paramagnetic centres are responsible for the spectrum often arises. Generally, if the system of lines can be subdivided into a number of subsystems, each of which is consistent with the laws governing the formation of the hyperfine structure, then these systems can be logically attributed to different paramagnetic centres. However, for poorly resolved signals, it is difficult to arrive at any definite findings by this procedure. The method of microwave line saturation is more promising here (although it by no means always works). For example, when the system contains alkyl and peroxy-radicals, the signal from the first can be "suppressed" by high microwave power[36]. In general, for a quantitative separation of a two-component signal, it is sufficient to obtain two linear

sections on the saturation curve, since the slopes of these lines are proportional to $n_1 + n_2$ and n_2 respectively. Finally the change in line form on saturation may be regarded as qualitative evidence of the presence of more than a single signal. The point is that at saturation the form of the lines due to paramagnetic centres should either remain unchanged (inhomogeneous lines) or it should broaden symmetrically (narrow, almost homogeneous lines with $\Delta H_1 > \Delta H$). When it is certain that there is no impurity causing dispersion, asymmetric deformation of the spectrum is evidence of the superposition of two or several signals with different T_1 and T_2 and different g-factors[37]. †

4. Quantum-chemical Analysis of ESR Spectra

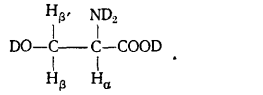
After formal mathematical analysis of the spectrum, we know in the general case all the constants of the magnetic interaction leading to the splitting or broadening of the ESR lines. Further analysis is based on the relations between the structure (electronic or geometrical) of the paramagnetic centres and the magnetic interaction obtained from the theory of ESR spectra. This theory has been described in detail in a number of monographs and reviews[1,38-43].

Only the following remarks need be made in addition to the data presented in the literature[1,38-43].

1. Refined effects involving changes in line form are increasingly used at the present time, after the publication of the elegant theoretical studies of Freed and Fraenkel[44], for the determination of the details of the electronic structure of radicals in liquid solutions[45].

2. When the g-factors are measured to within the 4th or 5th decimal place, they too can provide information about the chemical nature and the electronic structure of radicals. For example, Thomas[46] showed that peroxy-, hydroxy-, and alkyl radicals can be distinguished on the basis of the g-factors. Recently it has also been shown that the g-factor depends on temperature and the nature of the substituents in the radical[37,47].

We shall consider as a concluding example the "complete" analysis of the signal arising on γ-irradiation of α-substituted serine:



The spectrum, presented in Section III (Subsection 3) of this review, consists of 7 lines with the experimental intensities 12 : 16 : 21 : 31 : 25 : 18 : 20. The distances between the lines are approximately the same and equal to 13 Oe. The sum of the coefficients is

$$\frac{\Sigma A_m}{A_0} = \frac{143}{16} = 9 (= 3^2 \text{ or } 2^3).$$

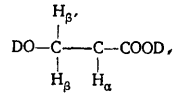
Since two nitrogen atoms cannot be present, it will be assumed that the hyperfine structure is due to three protons. Further,

$$\frac{A_2}{A_1} = \frac{18+16}{20+12} \simeq 1, \text{ i.e. } S_1 = 1; \; S_2 + S_3 = 2,$$

and therefore $S_1 = S_2 = S_3 = 1$. This means that the total splitting is

$$6 : 13 = 1 : 13 + (\alpha_2 + \alpha_3) \cdot 13 \text{ (oersteds)},$$

i.e. $\alpha_2 + \alpha_3 = 5$, so that $\alpha_2 \neq \alpha_3$. Hence $\alpha_2 = 2$ and $\alpha_3 = 3$. We conclude that the hyperfine structure is due to 3 non-equivalent protons with splittings of about 13.26 and 39 Oe. Such a situation can occur only in the radical



The splitting by the α-proton is evidently due to dipole–dipole nuclear spin interaction. For the β-splitting, we have $a_\beta \simeq 45 \rho_C^\pi \cos^2 \varphi$, and $\varphi_1 - \varphi_2 = <\text{HCH}$. With a favourable orientation, one of the β-splittings can reach 40 Oe, while the other should be small. Therefore it can be suggested that $a_\beta = 39$, $a_{\beta'} = 13$, and $a_\alpha = 26$ Oe. These figures are of course correct to within the line width and therefore the multiplicity of the splittings is only apparent. Next, with the aid of the Atlas[21], it is possible to obtain improved values of the constants: 40, 14, and 23 Oe respectively.

III. STUDY OF THE KINETICS AND MECHANISM OF CHEMICAL REACTIONS BY THE ESR METHOD

1. Gas-phase Reactions

The mechanism of gas-phase chemical reactions has been more thoroughly investigated than the mechanism of reactions in condensed phases. However, as regards the application of radiospectroscopic, methods the situation is reversed. This is probably because stable paramagnetic species do not exist in the gas phase (apart from the paramagnetic molecules of the type of O_2 and NO, which are not of particular chemical interest) and it is difficult to obtain high concentrations of active atoms and radicals. The ESR spectra recorded for H, O, S, K, Na, etc. atoms obtained in high-frequency discharges or by thermal dissociation are not themselves of significant interest to chemistry. A considerable advance took place after Voevodskii and coworkers[48] demonstrated the possibility of recording the ESR spectra of H atoms directly in the zone of a rarefied hydrogen flame in oxygen. According to Semenov and Hinshelwood's theory of branched-chain processes, the reaction $2H_2 + O_2 \rightarrow 2H_2O$ proceeds at low pressures via the active centres H, O, and OH, which should give rise to an ESR signal. By drawing the flames from the combustion zone into the resonator, Voevodskii and coworkers[48] succeeded in recording considerable (up to 10^{15} cm^{-3}) concentrations of H atoms. Later these investigations were continued vigorously at the Institute of Chemical Kinetics and Geology [? tentative interpretation of abbreviation (Ed. of Translation)] of the Siberian Division of the USSR Academy of Sciences and at the Institute of Chemical Physics of the USSR Academy of Sciences, where V. N. Kondrat'ev and A. B. Nalbandyan and coworkers succeeded in recording, using a special cell, the signals from O and OH in the $H_2 + O_2$ flame and then also the signals from the active centres in a number of branched-chain combustion reactions: H, O, and OH in the $CO + O_2$ flame with small amounts of added H_2; O and SO in the $S + O_2$ flame and O in the $CS_2 + O_2$ flame; H, O, OH, and SO in the $H_2S + O_2$ flame[49,50]. The ESR spectra of H, O, and OH generated in the combustion of hydrogen in oxygen, obtained by Nalbandyan and coworkers[49], are presented as an example in Fig. 9*a*. Using the calibration method discussed earlier (with O_2 and NO), the absolute concentrations

† A more complete discussion of the methods of analysis of ESR spectra of free radicals is given by Dobryakov and Lebedev[32].

of the active centres in experiments with different jet velocities (i.e. different reaction times) were calculated from these spectra (Fig. 9*b*). The same Figure also presents the variation of the concentrations of H, O, and OH with reaction time calculated on a computer from the known kinetic constants; comparison of the experimental and theoretical curves constitutes very convincing confirmation of the existing theories concerning the mechanism of the process. By changing the initial values of the constants k_i in the calculations, it is possible to achieve complete agreement with experiment and thereby improve (or redetermine) the fundamental kinetic constants.

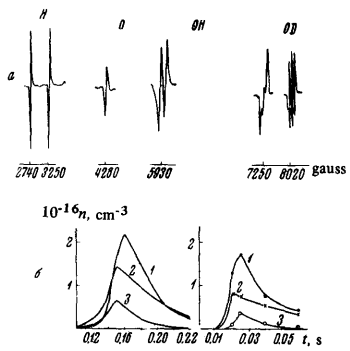


Figure 9. An example of the study of the mechanism of a gas-phase reaction—combustion of hydrogen in oxygen[49]: *a*) ESR spectra of active H, O, and OH centres; *b*) kinetic curves representing the variation of the concentration of the active centres with reaction time (comparison of the calculation with experiment); *1*) [O]; *2*) [H]; *3*) 10[OH].

However, the scope of the ESR method is not restricted to the confirmation and improvement of existing hypotheses. At the Institute of Chemical Physics of the USSR Academy of Sciences the ESR method has been used to justify certain new hypotheses of Semenov and Shilov concerning the role of chemical activation in branched-chain reactions[51]. Such a reaction should be a source of atomic concentrations (I and F) in excess of their equilibrium values. Indeed, by carrying out the reaction in the resonator, Shilov and coworkers[52] observed the spectra of atomic iodine (18 lines in the range between 3000 and 6300 Oe). The F and Cl signals were detected in the reaction between F_2 and C_2Cl_4 and the spectrum of atomic bromine was observed in the reaction between F_2 and CH_3Br.

No less interesting is the possibility of using ESR for the quantitative study of the fundamental stages of gas-phase reactions. Voevodskii and Panfilov[53] studied the reactions of atomic hydrogen with various hydrocarbons, by adding the latter to the $H_2 + O_2$ reaction zone and following the decrease of the intensity of the H signal as a function of the amount of additive and the extent of its combustion. This showed that, with rarefied flames, one hydrocarbon molecule can give rise to a chain of reactions involving the destruction of H atoms (from 2–3 for ethane to 75 for benzene). Nalbandyan and coworkers[54] established by the ESR method the pathway of the reaction between atomic oxygen and methanol:

$$O + CH_3OH \rightarrow \dot{O}H + \dot{C}H_2OH \quad \text{or} \quad \dot{O}H + \dot{C}H_3O \ .$$

For this purpose, they introduced CH_3OD or CD_3OH to $CO + O_2$ flames and determined the ratio [OD]/[OH] from the ESR signals. It was found that oxygen attacked mainly the methyl group.

Cold flames are not necessarily the only source of active species for the investigation of fundamental reactions. For example, Westenberg and coworkers in the USA made a quantitative study by the ESR method of the reaction of hydroxyl with OH, H_2, and CO, in which the very rapid reaction $H + NO_2 \rightarrow OH + NO$ served as a source of OH, and hydrogen was generated in the discharge[55]. In this investigation the rate constants for the reactions $OH + OH \rightarrow$, $OH + H_2 \rightarrow$, and $OH + CO \rightarrow$ at room temperature were determined with high accuracy and for the last two reactions the activation energies were also estimated (5.2 and 0.6 kcal mole^{-1}).

The active species produced in gas-phase reactions can be frozen out on cooled surfaces in order to accumulate them in high concentrations and to investigate in detail their ESR spectra. For example, by withdrawing atomic hydrogen from the discharge, it is possible to obtain phenyl radicals by the reaction[56]

$$H^{\cdot} + C_6H_6 \rightarrow H_2 + C_6H_5^{\cdot} \ .$$

The value of such preparations of radicals lies in the fact that their chemical structure is known *a priori* and the ESR spectra obtained can be used to identify the signals in other systems. A series of such radicals (propyl, butyl, heptyl, allyl, phenyl, and others) were obtained by Bennett and Thomas[57], with the aid of a technique involving a rotating cryostat and sodium beams, by the reaction

$$Na + RHal \rightarrow NaHal + R^{\cdot} \ .$$

The design of the experimental apparatus[57] is such that, by condensation of a third beam (in addition to RHal and Na), it is possible to study further reactions of the R$^{\cdot}$ radicals, for example:

$$R^{\cdot} + O_2 \rightarrow RO_2^{\cdot} \ ,$$
$$R^{\cdot} + C_2H_4 \rightarrow RCH_2CH_2^{\cdot} \ .$$

It was then found that oxygen reacts even at 77°K, while ethylene must be heated to 90–500°K. Bennett and Thomas[57] believe that, when account is taken of the gradual cooling of ethylene, it is possible to calculate the true rate constant for the reaction from the degree of conversion of R$^{\cdot}$ into $RCH_2CH_2^{\cdot}$ using an electronic computer. For example, they obtained in this way $E = 0.15$ kcal mole^{-1} for the reaction between C_6H_5 and C_2H_4. However, the accuracy of the determination of the constants by comparing the results of very cumbersome calculations with experiment is doubtful. Panfilov[58] applied the method involving the freezing out of the products from rarefied flames near the reaction zone in order to accumulate large amounts of free radicals. The sensitivity with respect to hydrogen atoms then increases at least by a factor of 50.

2. Liquid-phase Reactions

The paramagnetic centres (free radicals and radical-ions) in liquid and solid phases can have a wide variety of lifetimes, and henceforth we shall find it convenient to distinguish arbitrarily kinetically active and stable radicals. The application of electron spin resonance in chemistry began of course with the study of stable radicals and radical-ions. From stable radicals, interesting data were obtained on the electronic and geometrical structure, delocalisation of the unpaired electron, and internal motions

in molecules—data, which, as already stated, will not be discussed in great detail in the present review. From the standpoint of the kinetics and mechanism of chemical reactions, stable radicals as a rule do not behave as intermediate centres which can propagate real chemical reactions, but they can serve as models for the investigation of the most important problems of kinetics and reactivity. One of the first studies on the application of electron spin resonance in chemistry was the investigation of the rate of dissociation of hexaphenylethane into stable triphenylmethyl radicals, whereby it was possible to determine the heat of this reaction[59]. The capacity of stable radicals to recombine with active radicals makes it possible to follow the latter on the basis of the intensity of the ESR signal due to the stable radical. Diphenylpicrylhydrazyl is used particularly frequently as such a label. Buchachenko and others[39] investigated the kinetics of several hydrogen transfer reactions, such as the reaction between tri-t-butylphenoxyl and phenol, and determined the rate constant for the reactions and their dependence on the physical properties of the medium and the nature of the reacting molecules; these studies revealed a marked influence of hydrogen bonds on the rate constants. The effect of π-complex formation on the reaction rate has also been observed for aromatic radicals such as diphenylnitric oxide.

As far as the present author is aware, the first ESR study of "live" chemically active radicals directly in the course of the reaction was carried out by Shlyapintokh and Tsepalov with the present author's participation, using as an example the liquid-phase chain oxidation of hydrocarbons[60]. The "classical" mechanism of such a process is as follows:

$$\text{decomposition of initiator} \xrightarrow{W_i} 2\,R_i^{\cdot} \rightarrow 2R^{\cdot},$$

$$\left.\begin{array}{l} \rightarrow R^{\cdot} + O_2 \rightarrow RO_2^{\cdot} \\ RO_2^{\cdot} + RH \xrightarrow{k_2} ROOH + R^{\cdot} \end{array}\right| ,$$

$$RO_2^{\cdot} + RO_2^{\cdot} \xrightarrow{k_3} \text{destruction}.$$

As long as the reaction proceeds, a steady-state concentration of RO_2 (the $R^{\cdot}$ radicals are more active and their number is much less) should be maintained:

$$[RO_2^{\cdot}]_{st.} = \sqrt{\frac{W_i}{2k_3}}.$$

The rate of oxidation is then

$$W = k_2[RH][RO_2^{\cdot}] = \frac{k_2}{\sqrt{2k_3}}\sqrt{W_i}[RH].$$

Since W and W_i are known, the combined rate constants $k_2/\sqrt{2k_3}$ have been determined for a long time for many reactions. The ESR method permitted the measurement of the steady-state concentration $[RO_2^{\cdot}]$, which led to the determination of both rate constants for the process.

The ESR signal due to $RO_2^{\cdot}$ peroxy-radicals, which consists of a singlet with a displaced g-factor $g = 2.015$, was first recorded in the oxidation of cumene. The reaction at 60–100°C was performed directly in the resonator, where a special device ensured a continuous supply of an excess of oxygen (otherwise the relation specified above would be invalid). Fig. 10 presents the results of the measurement of $[RO_2^{\cdot}]_{st}$ and their comparison with the available data for cumene, obtained by the method of discontinuous illumination. Good agreement between the results showed that ESR can be used to determine the rate constants k_2 and k_3 also as an independent method; the rate constants for the oxidation of diphenylmethane, diphenylethane, etc. were obtained in this way. Somewhat later the signal due to $RO_2^{\cdot}$ in the oxidation of cumene was investigated independently in a jet by Thomas[61], who showed that the radicals may be stabilised by the formation of a complex with pyridine.

Nowadays the study of active radicals in the liquid phase (with purely chemical initiation) is almost always carried out in flow systems. Such systems are now widely known and their design has been frequently described. The flow rates are usually 10–100 cm sec^{-1} and the idle time (from the instant of the mixing of the reactants to the instant when the resonator is reached) amounts to hundredths of a second. The advantage of flow systems is that it is possible to maintain a high reaction rate over a long period (i.e. a high rate of initiation of active centres) without having to worry about the consumption of the reactants: while under static conditions the time constant for the recording of a signal should be much less than the lifetime of a radical or the time required for the consumption of the reactants, in a jet apparatus the time required for the mixture to flow out is the only limiting factor. It can be shown that under optimum conditions the gain in sensitivity is approximately $\sqrt{V_0 V_c}$, where V_0 is the volume of liquid which has passed through the resonator during the time when the signal was recorded and V_c the effective volume of the capillary in the resonator. Depending on the experiment, this gain does in fact reach 10–20.

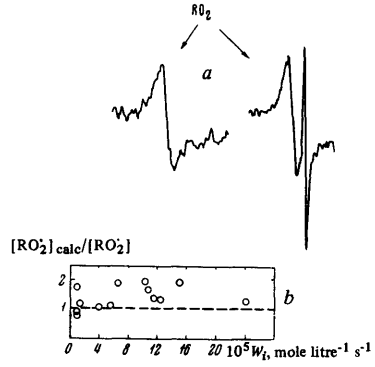


Figure 10. An example of the investigation of a liquid-phase reaction—chain oxidation of cumene[59]:
a) ESR spectra of cumenylperoxy-radicals; *b*) comparison of the calculated and experimental steady-state concentrations of radicals for different rates of initiation.

It has been shown in recent years that, it is possible with flow systems to obtain sufficient concentrations of active radicals at room temperature for recording ESR signals and for the investigation of the reactions of these radicals. In one of the first studies (using a jet) Dixon and Norman[62] obtained OH radicals by a reaction similar to Fenton's reaction:

$$Ti^{3+} + H_2O_2 \rightarrow Ti^{4+} + OH^{\cdot} + OH^{-}.$$

By adding various alcohols to the system, it is possible to observe the transformation of the $OH^{\cdot}$ spectrum into the signal of the alcohol radical, which is evidence of a reaction of the type

$$\dot{O}H + CH_3OH \rightarrow H_2O + \dot{C}H_2OH.$$

Analysis of the secondary ESR spectra established that in saturated alcohols a hydrogen atom is always split off from an α-carbon atom, while in unsaturated compounds the incorporation of OH at the double-bond was observed.

Similar flow ESR studies on radicals obtained by a one-electron transfer reaction are now being carried out on a wide scale. These are described in greater detail in the review by Waters[63]. They are undertaken mainly in order to elucidate the structure of the radicals formed and hence the mode of the fundamental reactions, but evidently the technique also permits quantitative kinetic studies.

For example, Blyumenfel'd and coworkers[64] studied the kinetics of the reactions of OH^- ions (in a flow system) with tetracyanoethylene, p-benzoquinone, and o-naphthoquinone, which lead to the formation of the corresponding radical-ions. The activation energies were determined and the effect of ionic strength and the addition of oxygen, hydrogen peroxide, and certain anions was investigated. It was shown that the effect of hydrogen peroxide depends on the pH of the medium, since molecular and ionic (HO_2^-) forms of hydrogen peroxide exist at different pH.

Another possibility of the kinetic and structural study of active radicals in the liquid phase was demonstrated by Fessenden and Schuler[65] in the USA, who directly recorded the spectra of C_2H_5 radicals (concentration about 4×10^{13} cm^{-3}, dose rate 10^8 mrad h^{-1}) with specially adapted apparatus in the radiolysis of liquid ethane. So far they have investigated the ESR spectra of a number of active radicals ranging from CH_3, C_2H_5, and FO_2 to 2,2-diethyl-1-methylbutyl. It has been shown that in all cases the destruction of radicals is probably determined by their diffusion, since a change in the viscosity of the solution (by the addition of glycerol) alters significantly the steady-state concentration of the radicals.

The possibilities for the investigation of short-lived species have also been greatly extended by a method involving the accumulation of the useful signal[66]. The principle of this method consists in synchronised n-fold recording of the signal with subsequent summation, as a result of which the sensitivity increases by a factor $\sqrt{n}$. The accumulation method in effect permits longer recording times without risk of a drift in the zero line, etc.; as far as one can judge from published data, this results in a sensitivity gain by a factor of 10. In the study of short-lived species, this method can be very effective only in combination with a flow system whereby long recording times can be achieved. On the other hand, the accumulator can be synchronised with a source of active species, as was done by Piette[67] (USA). Simultaneously with the flash of the photo-source or a specified time afterwards the instrument was switched on and the signal was recorded (at one point): at each point corresponding to specified time intervals from the start of the flash, the signal was recorded 25 times. This yielded a kinetic curve for the destruction of the cumenyloxy-radical (obtained by the photolysis of cumenyl hydroperoxide) at room temperature, where the reaction time constant amounts to about 0.03–0.05 s. Piette[67] hoped to obtain in this way the rate constant for the removal of hydrogen from solvent molecules, but the identity of the constants in cumene, ethylbenzene, and toluene shows that even at 20°C the reaction rates are limited by diffusion. The method described would probably permit the investigation of rapid reactions in any phase ("active" radicals are investigated as "stable" radicals), but it should be noted that we are unaware of any other publications on this question after Piette's communication in 1963, apart from the data presented in Soutif's review[40] on the study of rapid ($\tau = 0.01$ s) oxidation–reduction reactions of enzymes with the aid of a low-inertia jet system produced by the Varian Company. The method is admittedly fairly complex experimentally and it is not always possible (only for $\tau > 0.1$ s) to record the entire ESR spectrum, so that correct kinetic data can be obtained only when the line form coefficient does not change.

The kinetics of rapid processes have been investigated not only on the basis of the intensity of the ESR signals, but also on the basis of changes in line form. If as a result of a fast exchange reaction there is a transition of the unpaired electron from one molecule to another, and the transition frequency ν is greater than the line width (in terms of frequency units), a broadening of the lines in the spectrum is observed and then (when $\nu > \gamma a$) also blurring of the hyperfine structure. This phenomenon was used as early as 1954 by Weissman[68] to study the electron exchange between paramagnetic molecules. However, the reaction rate must not be less than 10^7–10^8 s^{-1}. [The author probably means that the bimolecular rate constants lie in the range 10^7–10^9 l mole^{-1} s^{-1} (Ed. of Translation)]

The rates of electron exchange in paramagnetic complexes can be studied similarly. Exchange of this type in aqueous solutions of copper(II) complexes of ethylenediamine, ammonia, etc. has been studied in detail by Voevodskii and Zamaraev[61]. The observed effect is the broadening of all the components of the quadruplet signal of Cu^{2+} ions with decrease of the concentration of copper $(Cu)_0$ and then

$$\Delta H_i = \Delta H_i^{\circ} + \frac{k_1}{[Cu]_0} .$$

It has been shown[69] that in the region of line narrowing due to exchange the principal contribution to the variable component of line width ΔH_i^* comes from the isotropic hyperfine interaction, and

$$\gamma \Delta H_i^{\bullet} = \frac{5}{4} \frac{a_{Cu}^2}{\omega_l} .$$

Thus $\omega_i = k_i[Cu]_0$ and the exchange rate constant can be determined at room temperature:

$$k_i \simeq 10^9 \text{ litre mole}^{-1} \text{ s}^{-1}.$$

Finally, the broadening of the ESR line may also be used to investigate a rapid kinetic process such as collisions in a liquid[39]. At high concentrations of stable radicals line broadening δH_l is observed, associated with exchange relaxation during collisions, as suggested by Buchachenko. If p is the probability of such relaxation on collision, then the exchange frequency is

$$\nu_i = \gamma \delta H_i = p k_2 \frac{Z n_r}{n_s} ,$$

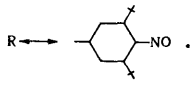
where k_2 is the number of collisions per unit time, n_r and n_S are the concentrations of the dissolved radicals and solvent molecules, and Z is the coordination number of the cage.

Assuming that $p \simeq 1$ and measuring the broadening δH_i at various n_r, it is thus possible to determine k_2 and, by making measurements at various temperatures, also the activation energy for the collisions. For 2,4,6-tri-t-butylphenoxyl in benzene and ethylbenzene, we have

$$k_2 = 3.5 \times 10^{-10} \exp\left(\frac{-2200}{RT}\right) \text{ cm}^3 \text{ s}^{-1}.$$

Recently Buchachenko and coworkers initiated on the investigation of collisions between the ends of the same molecules by studying line form changes in the ESR spectra

of biradicals and polyradicals[70]. They managed[70] to investigate the ESR spectra of nitrogen oxide radicals of the form R'–R, $ROOC(CH_2)_4COOR$, and others, where



It was found that the hyperfine structure corresponds to splitting by all the nitrogen atoms. Since in this case there is no possibility of electron delocalisation, it was suggested that electron exchange takes place as a result of the collisions between the paramagnetic ends of the molecule on the "claw" principle. In fact the frequency of the "averaging out" of the hyperfine structure proved to depend on the temperature and the structure of the central bridge. On the basis of a model involving special modulation of isotropic hyperfine interaction, developed by Freed and Fraenkel[44], it is possible to calculate further the frequency of the exchange interaction by the formula

$$\Delta H_i(\pm 1) - \Delta H_i(\pm 2) = \frac{1}{8}\gamma a_N^2/\nu_i ,$$

where $\Delta H_i(\pm 1)$ is the line width for the components with $\Delta m_N = \pm 1$ and ± 2 and a_N is the constant for the hyperfine splitting by nitrogen. It has been found that, for biradicals with pronounced exchange, ν_i is in the range 10^7–10^8 s^{-1}, with $\nu_i^0 \simeq 10^8$–10^9 s^{-1} and $E_i \simeq 1$–3.5 kcal mole^{-1}.

Thus application of electron spin resonance in the study of reactions in gas and liquid phases has been developing in the following ways.

1. The study of the mechanism of complex reaction by analysing (on the basis of the ESR spectra) the structure of the radicals formed in the process.
2. The determination of the rate constants for various radical reactions from the changes in the intensity of the ESR signals. Here the ESR method is used as a very sensitive and selective analytical procedure.
3. The determination of the mechanism and kinetic constants of fundamental reactions from the steady-state concentrations of the paramagnetic centres generated by the chemical reaction or external radiation (for a known rate of initiation).
4. Quantitative study of fast chemical and physicochemical processes (exchange reactions, collisions) on the basis of the changes in the width and form of ESR lines as a result of the paramagnetic relaxation induced by these processes.

3. Reactions in Solids

The study of chemical processes in the solid phase by the ESR method must be considered in greater detail, since in this field electron spin resonance is at present the most universal method for the investigation of fundamental reactions. The application of the ESR method led to the discovery of a very interesting field of radical chemistry, previously experimentally inaccessible, the study of radical reactions initiated by light, hard radiation, and chemical reactions in solids.

Examination of the specific questions associated with the application of electron spin resonance in photochemistry and radiation chemistry (the so called high-energy chemistry) is outside the scope of the present review. Here only the most interesting advances in this field will be briefly described (see Voevodskii's review[71]). By the stabilisation of radicals at low temperatures, the primary radicals formed on irradiation proved to be so stable that their chemical structure can be determined by the ESR method and sometimes it is possible to obtain information about their geometrical structure and orientation in the matrix. The study of the chemical nature of radiation damage at the instant when only a fraction of 10^{-8}–10^{-10} of all the molecules have been damaged leads of course to a completely new approach to the elucidation of the mechanism of this effect. ism of this effect.

A significant advance in these investigations was made in the Soviet Union in 1958–1960 when the formation of radicals during irradiation by ultraviolet light and fast electrons was investigated. Subsequent studies permitted a clear separation of the primary and secondary processes much more reliably than before, the determination of the radiation yields of chemical damage (i.e. the number of bond dissociations per 100 eV of energy absorbed), and the finding that the dominant chemical step in the radiolysis of hydrocarbons is the dissociation of C–H bonds. The same measurements led to unambiguous demonstration of energy migration preceding the primary dissociation and the formulation of the general hypothesis concerning the dependence of the radiation stability of hydrocarbons on structure (see, for example, Refs. 72 and 73). The structure of the ESR spectra showed that the breakdown of chemical compounds takes place with formation of the same radicals almost independently of the type of influence on the system —ranging from ionising irradiation and photo-irradiation to high-frequency discharge[74] and mechanical degradation[75]. It has also been shown that these influences can themselves initiate further reactions of the radicals produced[76–78].

In the field of purely photochemical investigations, the determination of the mechanism of a number of sensitised photochemical reactions[79], the observation and study of signals from triplet molecular states[80], and the study of two-quantum reactions[81] may be mentioned as interesting advances achieved with the aid of electron spin resonance. However, the application of electron spin resonance in the investigation of "stabilised" radicals is by no means confined to primary reaction steps. By studying the change in the ESR spectrum on heating the specimen, under the influence of various additives, and on repeated irradiation of the system with light of different wavelengths, etc., it is possible to obtain exceptionally interesting (both for radiation chemistry and for chemical kinetics in general) data on the mode and rates of the fundamental reactions in the solid phase, approximately in terms of the scheme formulated above for liquid-phase reactions. One of the most effective examples of reaction mechanism elucidation is the unambiguous demonstration of the existence of the so-called "adhesion" radical formed by a reaction of the type $H^{\cdot} + C_6H_6 \rightarrow C_6H_7^{\cdot}$.

The ESR spectrum of C_6H_7 radicals should of course differ sharply in its hyperfine structure (three lines with $a \simeq 46$ Oe × a quartet with $a \simeq 10$ Oe) from the spectrum obtained in the usual reaction of phenyl radicals C_6H_5 (four lines with $a = 18$ Oe × three lines each with $a = 8$ Oe).

C_6H_7 radicals were identified in solid benzene in 1961 (almost simultaneously) by Buben and coworkers[82], Fischer[83], and somewhat later by two groups of investigators in the USA[84,85]. Then it was shown, by direct experiments on the interaction between atomic hydrogen and benzene in the gas phase and the same reaction in the solid phase in a specially prepared solid matrix containing, at the beginning of the experiment, H atoms stabilised at 77 °K and molecules of aromatic compounds, that atomic hydrogen does indeed adhere to aromatic molecules. Analysis of the hyperfine structure of the ESR spectra of the radicals formed in the interaction of hydrogen atoms with various phenols actually permitted the determination of the site of adhesion of the H atom in each individual case[86].

One of the first quantitative studies on the kinetics of radical reactions was undertaken by Voevodskii et al.[85], who determined the rate constants for the reactions $R^{\cdot} + O_2 \rightarrow RO_2^{\cdot}$, $RO_2^{\cdot} \rightarrow R^{\cdot} + O_2$, etc. involving fluoroalkyl radicals in irradiated polytetrafluoroethylene and also measured the diffusion coefficients of O_2, H_2, and NO in Teflon and the radical recombination rate constants. Measurements were made at the same time of the heat of the reversible oxygen elimination reaction: $\Delta H_{R-O_2} = -6$ kcal mole^{-1}. Quite recently Janzen et al.[88] reported the measurement of the heats of the reaction of triphenylmethyl radicals with oxygen $\Delta H_{R-O_2} = -9$ kcal mole^{-1}. The radicals were obtained by γ-irradiation of triphenylacetic acid.

In principle, when the above methods are used for the measurement of concentration, the determination of kinetic curves (the time variation of the intensity of the signal) and their treatment by the usual methods of formal kinetics do not present special difficulties; for a unimolecular reaction, $\ln([R^{\cdot}]/[R^{\cdot}]_0) = -k_1 t$, for a bimolecular reaction, $1/[R] - 1/[R]_0 = k_2 t$, etc. However, further interpretation of these data does present a fundamental difficulty. The point is that when we measure by the ESR method say, the rate of disappearance of $R^{\cdot}$ radicals by the reaction $R^{\cdot} + R^{\cdot} \rightarrow M$ in a condensed phase, then the measured rate constant is not in general a fundamental constant. If we denote by k_m an average frequency of migration of the radical from one cage to another (diffusion coefficient $D = \frac{1}{6}\lambda^2 k_m$), then the number of collisions of radicals in a single cage with a volume V^* is $k_m V^*$. However, in the simplest case the probability of reaction is then $k_i/(k_i + k_m)$, where k_i is the rate constant for the intrinsic chemical reaction $|R^{\cdot} \ldots R^{\cdot}| \rightarrow M$ in the cage. Thus one measures the effective constant

$$k_2 = \frac{k_i k_m V^*}{k_i + k_m} . \qquad (4)$$

Consequently, for fast reaction where $k_i \gg k_m$, one measures essentially the rate constants for diffusion, $k_m V^* \sim D\lambda$, and only for slow reactions, where $k_i \ll k_m$, is it possible to measure the rate of the reaction itself. These considerations must be taken into account when electron spin resonance is used to study kinetic processes in solid and liquid phases. For reactions of stabilised radicals with mobile molecules, usually $k_m \gg k_i$, but when only stabilised radicals participate in the reaction, measurements are as a rule made on "diffusion" kinetics[89,90]. The cage effect can be taken into account similarly also in unimolecular decomposition reactions in the condensed phase; if k_i is the true rate constant for decomposition and k_t the rate constant for the reverse reaction in the cage, then the probability of emergence from the cage is $f = k_m/(k_m + k_t)$, and the measured rate constant for decomposition is

$$k_1 = \frac{k_i k_m}{k_m + k_t} = f k_i . \qquad (5)$$

With these simple hypotheses at our disposal, we shall examine in greater detail several examples of the application of electron spin resonance in the study of fundamental reactions in the solid phase.

a. Recombination Kinetics and Spatial Distribution of Paramagnetic Centres in the Solid Phase

When specimens containing free radicals accumulated in them at a low temperature (usually 77°K) are heated, the concentration of the radicals begins to decrease at certain temperatures and the kinetics of the recombination reaction can be studied from the decrease of the intensity of the ESR signal. It follows from the above considerations that it is then possible to measure the constants k_m, i.e. to obtain information about the mobility of free radicals.

Thus Buben and coworkers[91] measured the rate of recombination of radicals in irradiated cyclohexane near the gas-crystalline transition temperature state; the reaction kinetics were described by a second-order equation:

$$-\frac{dn}{dt} = k_2 n^2 \qquad (6)$$

and the measured radical mobility constant k_m agreed satisfactorily with the self-diffusion coefficients already available from NMR data. Similar measurements were made for a number of more complex organic substances and polymers at temperatures close to the melting point or a phase-transition temperature[87,89,92]; these measurements led to the hypothesis that in most cases the mobility of active centres is not determined by the diffusion of the molecules in the usual sense but by the transfer of the active centre by reactions of the type

$$R^{\cdot} + RH \rightarrow RH + R^{\cdot},$$
$$M^{-} + M \rightarrow M + M^{-} \quad \text{etc.}$$

However, in a very large number of cases the destruction of paramagnetic centres does not obey simple relations of the type of Eqn. (5). Two types of deviation are observed.

1. After heating at high initial radical concentrations, there is initially a sharp fall of the intensity of the ESR spectrum by a certain amount and then "steady-state" destruction begins described by Eqn. (6).[93]

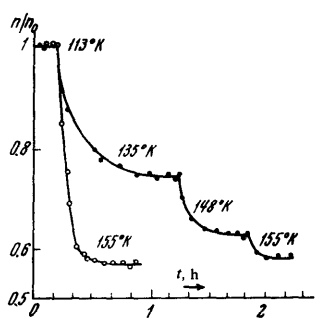


Figure 11. Stepwise kinetics of the recombination of free radicals in β-irradiated phenol[94].

2. The destruction of radicals at temperatures far removed from the melting point or a second-order phase transition is in most cases "stepwise", i.e. at each temperature a definite concentration of paramagnetic centres remains[94]. The experimental curves illustrating these phenomena are presented in Figs. 11 and 12. The behaviour of the destruction curves over a wide range of initial concentrations n_0 is independent of the latter, i.e. the curves can be made to coincide after replotting in terms of the coordinates n/n_0 and t. Nevertheless, the rate of normal recombination [Eqn. (6)] should depend significantly on n_0.

Both these kinetic phenomena can be explained if it is assumed that the paramagnetic centres are not distributed uniformly throughout the solid substance but in groups or

pairs[93,94]. Consequently the concentration of paramagnetic centres determined from the ESR signals does not reflect their true density in the specimen. Thus, we return to the problem formulated in Section II (Subsection 2)—the problem of the measurement of local concentrations of paramagnetic species. Attempts at such estimates were made on the basis of the measurement of the dipole–dipole contribution to the ESR line width either directly[10] or by the method of successive saturation[14,17,18] and the electron spin-echo method[13]. In general, these measurements confirmed (so far semiquantitatively) the conclusion concerning the possibility of non-uniform distribution of radicals in irradiated solids. Similar non-uniform distribution of paramagnetic centres has been detected in frozen solutions of stable radicals (diphenylpicrylhydrazyl[95]) and in a non-radical system[96] (frozen solutions of the ions Mn^{2+} and Gd^{2+}), where the non-uniformity is due to segregation. The study of this effect is also very important chemically.

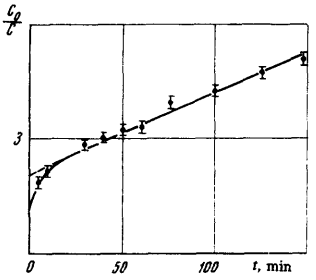


Figure 12. Kinetics of the recombination of free radicals in γ-irradiated polyethylene (according to the data of A.Arvia et al., see Lebedev[93]) [This is probably a reference to A.J.Arvia, F.Cracco, and M.Dole, J.Chem.Phys., 37, 2449)1962) (Ed. of Translation).]

At the present time new data have been obtained by the ESR method, concerning the non-uniform distribution of "heavy" radiation defects and also of dissolved paramagnetic centres in crystallising systems.

b. H–D Exchange Reactions of Free Radicals in Irradiated Amino-Acid Single Crystals.

Isotope exchange is one of the direct methods for the investigation of mechanism and reactivity and therefore the present author attaches great interest to the data published recently concerning the solid-phase H–D exchange in free radicals stabilised in irradiated single crystals of amino-acids—alanine[97], aspartic acid[98], and (indirect data) glycine[99]. The authors of these investigations made no attempt to explain in detail the chemical mechanism of the reactions, but it was shown that the ESR method reveals the successive substitution of H atoms in the aliphatic chain in partially deuteriated (at the sites containing mobile protons) amino-acids, and a detailed investigation of the kinetics of the changes in the ESR spectra made gave the kinetic constant for the reactions of aspartic acid. Together with Almanov, the present author made a similar study[100] of possible H–D exchange in the previously uninvestigated single crystals of DL-serine (monoclinic system, symmetry class C_{2h}, monoclinic angle 106°) grown from a solution in 90% D_2O:

$$DO{-}CH_2{-}CH(ND_3^+){-}CO_2^-.$$

After irradiation at room temperature from a cobalt-60 γ-source with a dose of about 20 mrad, the ESR spectrum was as in Fig. 13*a*, which corresponds (see Section II, Subsection 4) to radicals of the type

$$DO{-}CH_2{-}\dot{C}H{-}COOD.$$

In the orientation corresponding to $H_0 \parallel b$, $\Delta H_\alpha = 23$ Oe, $\Delta H_\beta = 40$ Oe, and $\Delta H_{\beta'} = 14$ Oe. On further heating of the single crystal to 50–100°C, the ESR spectra changed significantly, as shown in Fig. 13*c*, the total concentration of radicals not decreasing by more than 20%. Analysis of the structure of the ESR spectra presented in Fig. 13 indicates the occurrence of the following consecutive reactions:

$$-CH_2{-}CH_2 \xrightarrow{(1)} CHD{-}CH{-} \xrightarrow{(2)} -CDH{-}CD{-} \xrightarrow{(3)} -CD_2{-}CD-.$$

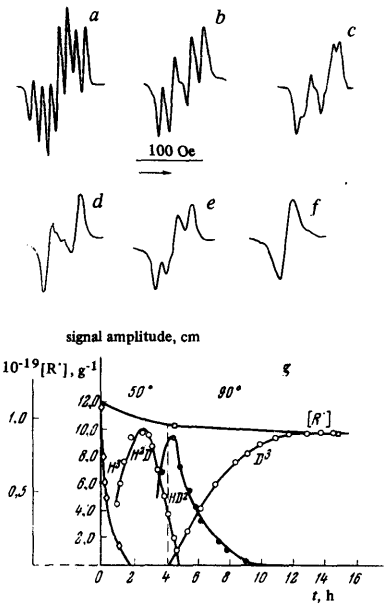


Figure 13. An example of the investigation of H–D exchange in the solid phase—exchange undergone by free radicals in γ-irradiated DL-serine[98]:
a) ESR spectrum obtained after γ-irradiation of a deuteriated single crystal at room temperature; *b*)–*f*) changes in the spectrum as a result of successive heat treatment for 2 h at 50°C (*b*), 4 h at 50°C (*c*), 2 h at 90°C (*d*), 4 h at 90°C (*e*), and 10 h at 90°C (*f*); *g*) kinetics of the change in the overall concentration of R· and the concentration of radicals corresponding to different degrees of substitution of α- and β-protons by deuterium.

Fig. 13*g* shows the kinetic curves determined from the intensities of the corresponding components of the hyperfine structure, which also indicate the occurrence of the irreversible consecutive reactions $H^3 \rightarrow H^2D \rightarrow HD^2 \rightarrow D^3$. The variation of the reaction rate with temperature corresponds to $E_1 \simeq 25$ kcal mole^{-1} and $k_1^0 \simeq 5 \times 10^{13}$ s^{-1} for reactions (2) and (3); according to previous data, E does not differ appreciably from E_1, but k^0 is significantly smaller than k_1^0. The findings described here are thus

almost completely consistent with the results obtained earlier for alanine and aspartic acid[97,98].

On the basis of the available data[97-100], the following interesting features of H–D exchange reactions in the solid phase may be noted.

1. The reaction involves free radicals only.
2. The reaction is stereospecific, i.e. the protons located in different positions relative to the free valence are substituted in a definite sequence. Of the two β-protons, the one whose hyperfine splitting constant is smaller is substituted first.
3. In irradiated methylsuccinic acid the reaction virtually does not take place, although the radical formed is quite similar (H^3).
4. The reactions are irreversible up to the complete substitution of all the hydrogen atoms in the radical.

The last finding immediately excludes the hypothesis that the exchange takes place within the limits of a single molecule or crystal unit cell: since $\Delta G \simeq 0$, equilibrium should then be established between the deuteriated and the initial radicals. It must be postulated that the exchange reaction is of second order and the concentration of H donors is much higher than the concentration of radicals, i.e. there is a possibility of the transfer of deuterium and hydrogen atoms over long distances, a possibility which has been frequently postulated to account for the kinetics of radical reactions in solids[74,90]. The present author believes that in the present concrete case the transfer of deuterium atoms can be achieved via molecules of D_2O of crystallisation, which are known[101] to be entrained in crystalline amino-acids in an amount approximately equal to the number of molecules of the acid and which probably acquire diffusional mobility at 50–100°C. Then the exchange mechanism can be represented thus:

$$-CH_2-\dot{C}H- + D_2O \rightarrow -CH_2-\underset{\diagdown\,\diagup}{\overset{O}{CH}}-\underset{D\quad D}{} \rightarrow -\dot{C}H-CHD + HDO,$$

$$-\dot{C}H-CHD- + D_2O \rightarrow -CHD-\dot{C}D- + HDO,$$

$$-CHD-\dot{C}D- + D_2O \rightarrow -CD_2-\dot{C}D- + HDO.$$

The suggested reaction mechanism explains in broad outline the experimental findings 1–4, but is of course only a preliminary hypothesis. In principle, the role of D_2O can be fulfilled by D_2 or ND_3 (however, $[D_2]$, and $[ND_3] \simeq [R^\cdot]$, while $[D_2O] \gg [R^\cdot]$). On the other hand, the general conclusion concerning the possibility of a solid-phase bimolecular exchange reaction in which the rate-limiting stage is the transfer of hydrogen seems to be adequately justified. Further study of the kinetics of such reactions can provide valuable information about fundamental processes in the solid phase.

c. Kinetics of the Polymerisation of the Oligomers of Acrylate Esters

The description of the application of electron spin resonance in the study of polymerisation reactions might have constituted a large section of the present review‡. One may refer to studies on growing-chain radicals[102,103], the cross-linking of polymers under the action of radiation[104], etc. However, here this problem is examined only as part of the general problem of solid-phase reactions, using a single concrete example.

‡ See, for example, the review of Buchachenko et al. on electron spin resonance in polymers[114].

Korolev et al.[105] made a series of studies by the ESR method on the initiation of polymerisation and polymerisation kinetics at advanced stages. They investigated the ESR signals from radicals entrained in the course of thermo- or photo-initiation of the three-dimensional polymerisation of acrylate ester oligomers—such as butylene glycol dimethylacrylate and others. They used phenyl peroxide, azobisisobutyronitrile, etc. as initiators. The typical radical accumulation curve in thermally initiated polymerisation has a maximum, according to Smirnov et al.[105] The decrease of the intensity of the ESR signal after prolonged periods is evidently associated with the disappearance of the initiator. In accordance with Eqn. (5) derived above, the rate of decomposition is

$$W_i = fk_i[I]_0 e^{-k_i t},$$

where f is the efficiency of the initiation and $[I] = [I]_0 e^{-k_i t}$ is the initiator concentration. The equation describing the accumulation of radicals is

$$\frac{d[R^\cdot]}{dt} = W_i - k_2[R^\cdot]^2,$$

whence

$$[R^\cdot] = \sqrt{\frac{W_i}{k_2}}\tanh\sqrt{W_i k_2}t),$$

at small values of t, i.e. at the beginning of the curve we have

$$[R^\cdot] \simeq W_i t = fk_i[I_0].$$

For large values of t, one may assume that $\tanh(\sqrt{W_i k_2}t \simeq 1$: then $\ln[R^\cdot] = \text{const.} - \frac{1}{2}k_i t$.

Hence it is clear that one can estimate from the experimental curve a quantity which is very important chemically—the initiation efficiency. Admittedly, it is assumed that the radicals which did not emerge from the cage give rise to the same initiator I molecule. The photo-initiation kinetics can be investigated similarly. In particular, Smirnov et al.[105] concluded that polymerisation in the systems investigated is initiated by a radical-acceptor mechanism of the type

$$R_I^\cdot + \underset{|}{CH_2} \rightarrow R_IH + \underset{|}{\dot{C}H}.$$

This conclusion is confirmed by the ESR spectra of radicals (doublet with a splitting of 22.5 Oe) recorded at −10°C. On raising the temperature to 80°C, it is converted into a signal of the growing-chain radical, which is subsequently in fact entrained in the polymer.

d. Detection of Radical Pairs and the Study of the Cage Effect

The characteristics of chemical reactions in condensed phases can be associated to a large extent with the Franck–Rabinowitch cage effect, which so far has been inferred solely from kinetic data, since there exists no direct method for the detection of species in the "cage". Nevertheless, in principle the ESR method makes it possible to distinguish the free radicals in the "cage" from isolated radicals, since the mutual approach of paramagnetic centres to a distance up to 5–10 Å should entail the appearance in the ESR spectrum of dipole–dipole and exchange interaction of electron spins. Recently data have been published on ESR spectra of radical pairs stable at the temperature of the measurement for large concentrations of radicals entrained in single crystals[106,107] and glasses[108].

The radical pairs formed in the cage during a real chemical process cannot of course be stable, but, if their steady-state concentration is not too low, it is evident from what has been said above that in principle they might be detected by the ESR method. Recently the present author succeeded in showing[109] that "active" radical pairs can indeed be detected directly during the low-temperature photochemical decomposition of azobisisobutyronitrile (AIBN) and in measuring the probability of the emergence of the radicals from the "cage" by the ESR method. AIBN is known to decompose readily into two radicals with evolution of a nitrogen molecule; by virtue of the high rate of initiation of the pairs and the relatively large distance between the radicals in the cage, relatively high concentrations of pairs can be obtained in this case. Earlier the present author observed together with Shuvalov and Zhuravleva[110] that, apart from the ESR spectrum due to the radicals $(CH_3)_2C(CN)$, which consists of a septet (a_H = 21 Oe) of triplets (a_N = 7 Oe) (see the analysis of this spectrum in Fig. 14), a signal unusual for this system, namely a doublet with a splitting of about 160 Oe and an additional hyperfine structure, appears in the first minutes of the photolysis of AIBN. Next the author postulated that this signal is due to radicals which failed to emerge from the cage, and carried out spectroscopic and kinetic studies which confirmed this hypothesis.

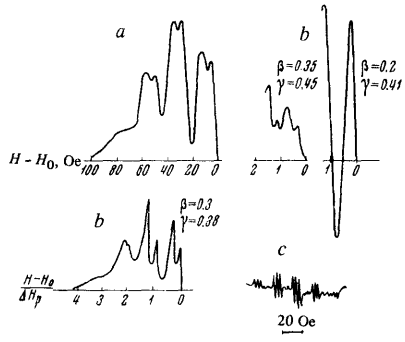


Figure 14. Analysis of the ESR spectrum of the cyanoisopropyl radical based on the comparison with calculated line form: *a*) ESR spectrum of the radicals produced in the photolysis of azobisisobutyronitrile; *b*) calculated spectra corresponding to different ratios $\beta = \Delta H_n/a_N$ and $\gamma = a_N/a_H$; *c*) spectrum obtained in the thermal decomposition of azobisisobutyronitrile in the liquid phase[110].

AIBN specimens obtained in the form of a crystalline powder were photolysed with light from a DRSh lamp in the resonator of an EPR-2 spectrometer of the Institute of Chemical Physics at 77°K; to prevent heating by the light, the tube with the specimen was filled with liquid nitrogen. When the light was switched on (effective spectrum with $\lambda < 330$ nm), the signal I shown in Fig. 15*a* appeared—a doublet with a splitting of 160 Oe and an additional hyperfine structure consisting of 11 lines with intensity ratios of approximately 1 : 5 : 20 : 45 : 75 : 90 : 75... In the course of further photolysis this spectrum is accompanied by the appearance of another (Fig. 15*b*), which is stable at 77°K, while the doublet signal disappears 30 s after the light is switched off (Fig. 15*c*). When the experiments were performed with isolated crystals, there appeared in spectrum I yet another similar system of lines II, the doublet splitting in which changed from 0 to 300 Oe on rotating the crystal. Spectra I and II can be attributed to the radical pair (R'...R'), since here one should in fact observe spin-spin splitting, changing on rotation of the single crystal from $D_\perp = D_0$ to $D_\parallel = -2D_0$ according to the law $D = D_0(1-3\cos^2\theta)$. The orientation-independent signal in the single crystal can be due to an admixture of an amorphous phase or other causes, which are not discussed here, since we did not have at our disposal "true" single crystals with indexed crystallographic axes. Therefore the principal conclusions were based on the study of the signals I in polyoriented specimens.

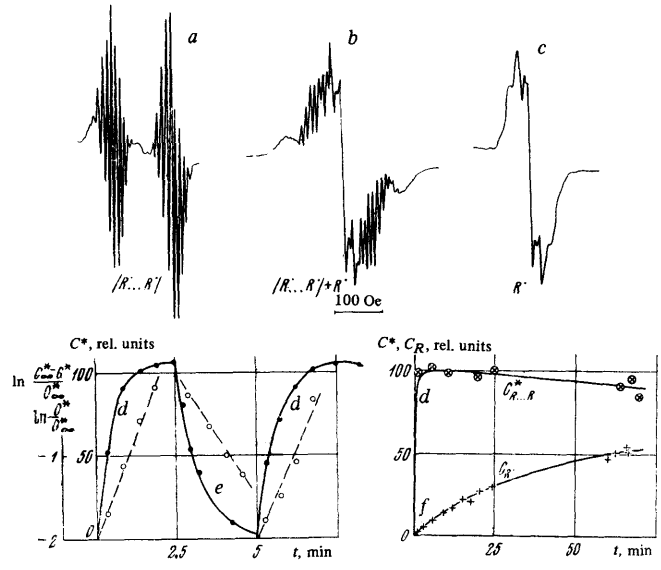


Figure 15. ESR spectra (*a*, *b*) and the kinetics of the formation (*d*) and destruction (*e*) of radical pairs and radicals [*c*) spectrum; *f*) accumulation kinetics] in the photolytic breakdown of azobisisobutyronitrile[109].

At first sight the possibility of the observation of a strongly anisotropic signal in polycrystalline specimens appear strange. However, the point is that in the case of axial splitting anisotropy, which obtains here, the probability of perpendicular orientations is greatly enhanced and the spectrum shows almost only the lines corresponding to this orientation. Fig. 16*b* shows a calculated ESR spectrum made up of "asymmetric" lines (without taking into account the additional hyperfine structure)[25]. This spectrum agrees satisfactorily with the experimentally observed spectrum of AIBN powder when the latter is recorded over a wide range of scan of the magnetic field and the hyperfine structure is artificially "blurred" (Fig. 16*a*). Analysis of the experimental spectra showed that the splitting of 160 Oe observed in experiments with AIBN powder corresponds to $D_\perp$, which in turn corresponds to dipole–dipole interaction between electron spins over a distance of 5.6 Å, approximately the same as the distance between the radicals in the initial molecule. Finally, the additional hyperfine structure can be due to splitting by the 12 protons present in the pair (only 11 lines are shown, since the two

extreme components have an intensity lower by a factor of 10; the calculated intensity ratios of the observed 11 components, 12 : 66 : 220 : 495 : 792 : 924 : 792:..., are in agreement with experiment). It is interesting that the splitting by the protons is smaller by a factor of 2 than in isolated radicals and that all the protons are equivalent, in agreement with the theoretical postulate of Kurita and Kashiwagi[107], according to which the structure of the spectrum of the radical pair is described by the relation (taking into account the fact that $a_N \ll a_H$):

$$H = \frac{h\nu}{g\beta} \pm \frac{D}{2} - \frac{1}{2}\sum a_H m_H .$$

In contrast to the work of Kurita and Kashiwagi[107], who investigated stable radical pairs in dimethylglyoxime, the present author failed to observe signals corresponding to $\Delta M_S = 2$, which is probably due to an insufficient concentration of the pairs and the fact that the intensity of the signal with $\Delta M_S = 2$ is smaller approximately by three powers of 10 than the intensity of the main spectrum.

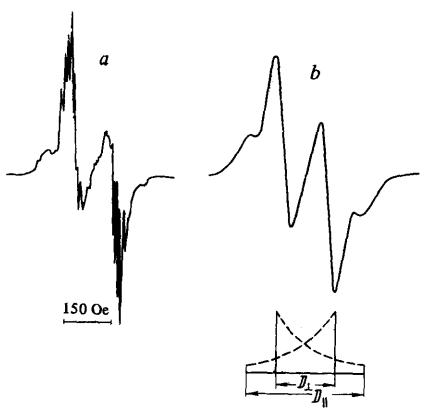


Figure 16. Experimental and calculated (without hyperfine structure) line form of the ESR signal due to polyoriented radical pairs.

It is also interesting to note that in their experiments on the low-temperature photolysis of AIBN, Ayscough et al.[111] obtained an ESR spectrum which they interpreted as a quintet with a splitting of 60–70 Oe and attributed to the radical R–N=N·. The present author regards this interpretation as insufficiently unambiguous, since the spectrum recorded with the signal only slightly greater than the noise can constitute the sum of the spectra of the "pair" |R·...R·| and isolated cyanoisopropyl radicals (see Fig. 15*c*).

Fig. 15 presents the result of an investigation of the kinetics of the accumulation and destruction of "pairs" and also the accumulation of radicals; these results are consistent with the above hypotheses. The transformed curves in Fig. 16*e*–16*f* show that the accumulation of "pairs" on illumination and their disappearance in the dark are consistent with destruction by a first-order reaction with approximately the same rate constant $k_1 = 0.03 \pm 0.01$ s^{-1}. On the basis of the usual kinetic mechanism of "cage" decomposition [Eqn. (5)], it is not difficult to show that the ratio of the initial yields of individuals radicals and radical pairs is equal to the probability of the emergence of the radicals from the cage. Nor can one exclude the possibility that the photochemical decomposition of AIBN takes place by the mechanism

$$M \rightsquigarrow \underset{\text{"hot" pair}}{|R\cdots R|^*} \rightarrow R + R$$
$$\downarrow$$
$$M' \leftarrow \underset{\text{thermolysed pair}}{|R\cdots R|}$$

which differs somewhat from the "classical" mechanism, but such a change in mechanism does not affect the determination of f. From the data in Figs. 15*d*–15*f*, one can estimate that $f = (1\text{–}3) \times 10^{-2}$, which is in satisfactory agreement with the value of f obtained by Smirnov et al.[105] for the decomposition of AIBN in polymeric matrices (admittedly for very much higher temperatures).

The following equation has been obtained for the rate constant for the destruction of cyanoisopropyl radicals in the AIBN cage in the temperature range 63–77 °K:[112]

$$k \simeq 10^8 \exp(-3500/RT)\ (s^{-1}).$$

Thus with AIBN as an example, it proved possible to investigate directly the cage effect by the ESR method§. The possibility of direct determination of the probability of emergence from the cage and the constants for the decomposition and entrainment of radical pairs can prove extremely useful for the elucidation of the detailed mechanism of the cage effect. To an equal extent, it is interesting to investigate the structure of the spectra of radical pairs, the electronic structure of which has much in common with the electronic structures of both molecules in the triplet state and activated complexes in recombination–dissociation reactions.

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The scope of the application of electron spin resonance in the study of the kinetics and mechanism of chemical processes has been examined. A fairly wide range of problems has been covered, but certain specific questions, such as the study of catalysis and reactions on the surface, electrochemical reactions, biological processes, etc. have not been touched upon at all. It should be understood that the separation of problems associated with the study of the kinetics and mechanism of reactions from structural and chemical investigations is purely arbitrary. Frequently such investigations are carried out simultaneously. In particular, one of the most interesting problems of chemical physics involves the comparison of data on the structure and kinetics (reactivity) of free radicals. Electron spin resonance is a very suitable method for this purpose, because for example, it makes it possible to measure the spin density of the unpaired electron ρ_S at different centres (the spin density is in some measure usually related to electron density) and to determine simultaneously the rate constants for the reactions of the atoms split off. In principle, one may hope to observe a correlation between these two quantities, which would permit the prediction of chemical activity on the basis of hyperfine structure data. However, sufficient quantitative data are not as yet available for a test of such a correlation. Thus in the studies on H–D exchange[97–100] described towards the end of Section III the hyperfine structure constants and H–D exchange rate constants for all the protons (α, β, and β') of the aliphatic chain were determined for three substances. However, the difference in the rates is due to the differences

§ At the present time radical pairs have been investigated also in the decomposition of tetraphenylhydrazine and certain organic peroxides[115].

between the pre-exponential factors and is probably associated with geometrical factors. The activation energies E (the correlation of which with ρ_S appears most likely) are indistinguishable because of the considerable error in the determination. Admittedly, more promising results have also been published recently. For example, Solodovnikov et al.[113] investigated by the ESR method the distribution of spin density in 4-aryl-2,6-di-t-butylphenoxy-radicals simultaneously with the investigation of the reactivity of these radicals in reactions with peroxides and oxygen. The measured activation energies range from 9.9 to 11.9 kcal mole^{-1}, the accuracy being 0.2 kcal mole^{-1}. Carbon-13 has been used to measure the spin density at a reaction centre—the tertiary carbon atom of the C_6H_5–C_6H_5 bond. A fairly clear correlation between ρ_S and E was obtained in this investigation.

Even the artificially restricted range of problems which could be discussed here appears to show quite convincingly that the ESR method has already found wide application in chemical studies but that its possibilities are by no means completely discovered. Further development of the application of electron spin resonance in chemistry will probably involve both thorough and comprehensive use of the information contained in the ESR spectra and a rational combination of the ESR method and other physical and chemical techniques.

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